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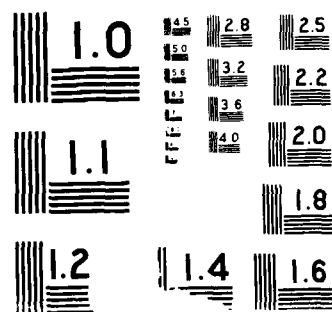
BRIEF REPORT ON A VISIT CONFERENCE AND DISCUSSIONS WITH 1/1  
DR EVERETT E GILB (U) BONN UNIV (GERMANY F R)  
H WAMHOFF 29 JUL 86 DAJA45-85-C-0016

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INSTITUT FÜR ORGANISCHE CHEMIE  
UND BIOCHEMIE  
DER UNIVERSITÄT BONN

Prof. Dr. H. Wamhoff

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Ref.: Contract No. DAJA 45-85-C-0016  
"New Synthetic Approaches to TAT"

Dear Dr. Squire,

in the following I am sending you a

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BRIEF REPORT

ON A VISIT, CONFERENCE, AND DISCUSSIONS WITH DR. EVERETT E. GILBERT  
US-ARMY ARMAMENT, MUNITIONS AND CHEMICAL COMMAND, PICATINNY AREAL,  
DOVER/NJ ON JULY 21, 1986

Arrival time (by rental car) at Picatinny Areal: 9:30 a.m.

Departure time: 2:00 p.m.

Dr. Everett E. Gilbert received me at the Visitors Entrance of  
Picatinny Areal and we went in his car to the Chemistry Laboratory

After arrival we had an intense, stimulating and fruitful conference  
where I reported to Dr. Gilbert and one of his colleagues on our  
recent results in novel TAT syntheses. The overhead folios shown  
during my seminar are attached to this report.

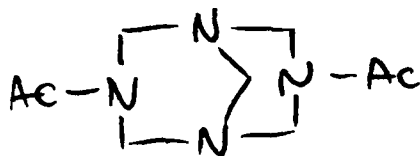
As a result, new promising ways for the synthesis of TAT have been  
discussed in detail, and on the base of an exchange of results ob-  
tained meanwhile both in our laboratories in Bonn and in the labo-  
ratories of Dr. Gilbert Dover/NJ, numerous new experiments are to  
follow, which will be described also in the FOURTH INTERIM REPORT

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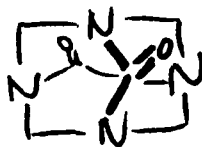
(ITEM 0004), which follows within the next weeks.

Especially, more interest should be cast on DAPT.

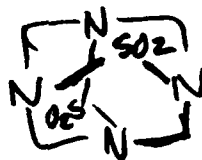


which can be easily obtained by a procedure of E.E. Gilbert et al. Propellants & Explosives 6, 67 (1981) and references cited therein; all methods of destructing the internal methylene bridge should be studied in detail on this target molecule.

Furthermore, a reaction of urea with formaldehyde is strongly suggested which should afford a carbonyl-bridged urotropine, such as:




Special interest should also be paid to a well known tetramethylene-disulfotetramine described by Hecht and Henecka, Angew.Chem. 61, 365 (1949):



With the aid of trivalent phosphorus compounds (deoxygenation) or by photochemical extrusion reaction (selective excitation) transformations of this highly bioactive compound could be studied in detail but all work on this compound must be carried out very cautiously, due to its high convulsive activity.

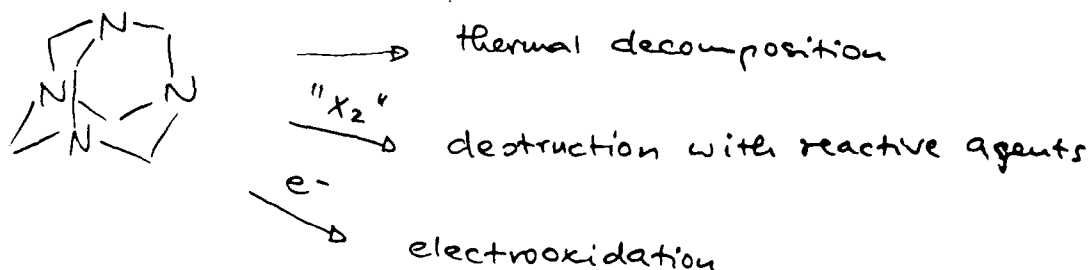
With best regards,

  
(Prof. Dr. H. Wamhoff)

## Strategies for TAT Synthesis

### A) UROTOPINE ROUTE

#### (a) Partial Destruction of Urotropine



#### (b) Controlled Approach by Classical Urotropine Synthesis



#### (c) Oxo-TAT Approaches

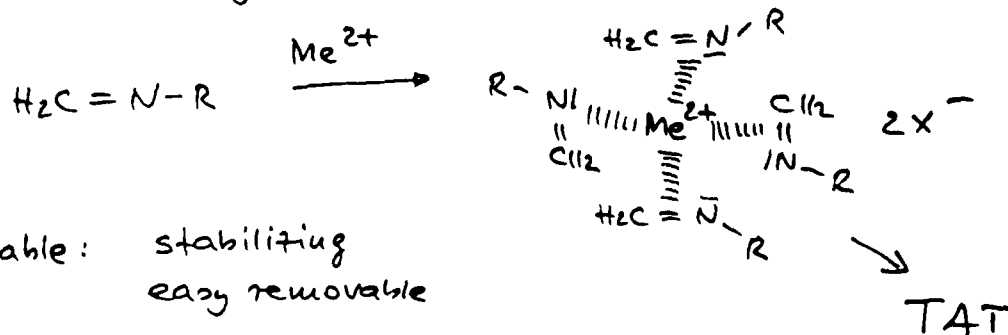
## Strategies for TAT Synthesis

### B) METHYLENEIMINE ROUTE

#### (d) Generation of Methyleneimines

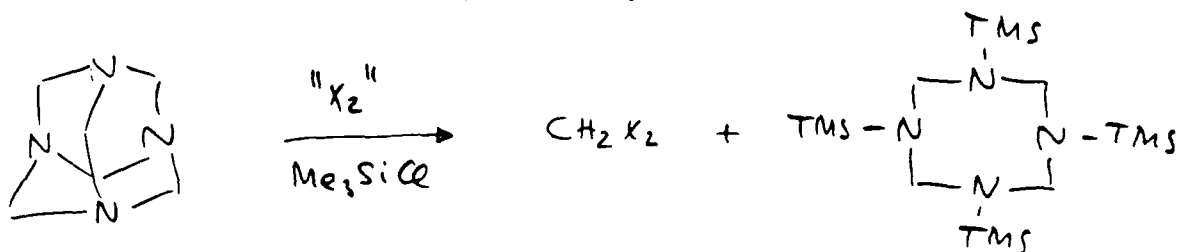
$\Rightarrow$  in free state (only with suitable <sup>\*</sup> substituents)

$\Rightarrow$  in situ generation and interception



<sup>\*</sup> suitable: stabilizing  
easy removable

## Urotropine Degradation



"X<sub>2</sub>" =  $\text{POCl}_3$

$\text{PPh}_3 / \text{C}_2\text{Cl}_6 \Rightarrow \text{Cl}_2\text{PPh}_3$

$\text{PPh}_3 / \text{CCl}_4 \Rightarrow \text{Ph}_3\text{P}^+ \cdots \text{Cl}^- \cdots \text{CCl}_3$

$\text{PX}_5$  no selective degradation

$\text{Br}_2\text{PPh}_3$  U. remains stable

... or total destruction

( $\Rightarrow \text{NH}_4\text{X}$ )

Refluxing with  $\text{TMSCl}$  (also autoclave):  $\times$

N-Chlorosuccinimide /  $\text{CCl}_4$  at  $\text{RT}^\circ$ :  $\times$

$\Delta$  reflux: total destruction

planned:  $\text{MeCN} / \text{NCS}$   $-10^\circ \rightarrow \text{RT}^\circ$  longer period

## Electrooxidative Degradation of Urotropine

First orientating experiments

undivided cell:  $\text{MeOH} - \text{NaClO}_4 - 1\text{V}$  : no effect

$\text{MeOH} - \text{NaClO}_4 - 10\text{V}$  : degradation

$\Rightarrow$  inorganic products

Critical voltage range: 5-10 V

galvanostatic experiment: current constant, 2 electrodes  
voltage varying

now under investigation: (in Metrohm cells)

potentiostatic experiment: current constant  
voltage constant  
against reference electrode

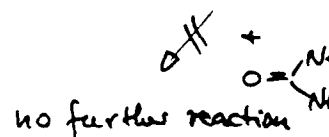
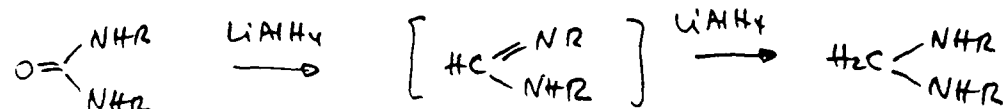
$\text{MeCN} / \sim 5\text{V} \Rightarrow$  Urotropine recovered + substances

$\text{MeCN} / \text{Ac}_2\text{O} / \sim 5\text{V}$  in progress

# Carbonyl Analogs of TAT



Reduction of Ureas:

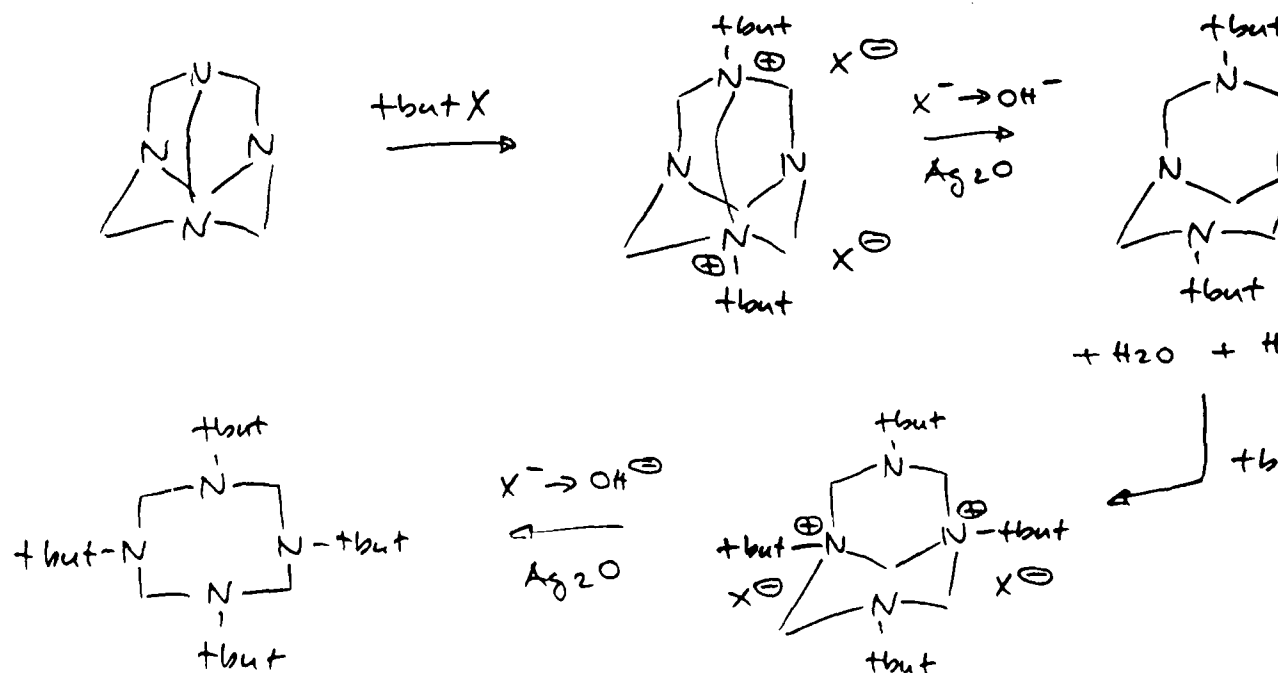


planned experiment:



Lit.: G. Lettleri, A. Larizza, G. Brancaccio, F. Monforte, Atti Soc. Peloritana Sci. Fis. Mat. Nat. 24 (1) 77 (1978); C.A. 92, 94028 (1978)

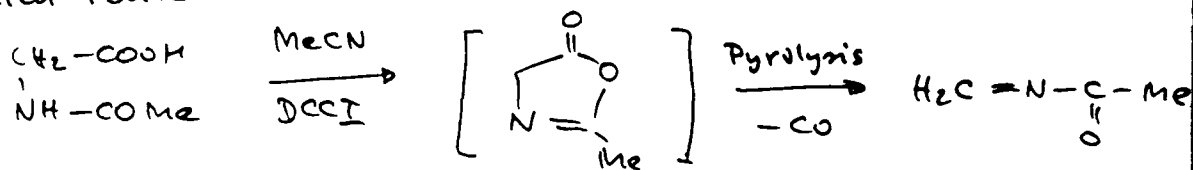
## Hofmann Degradation



experiment currently under investigation

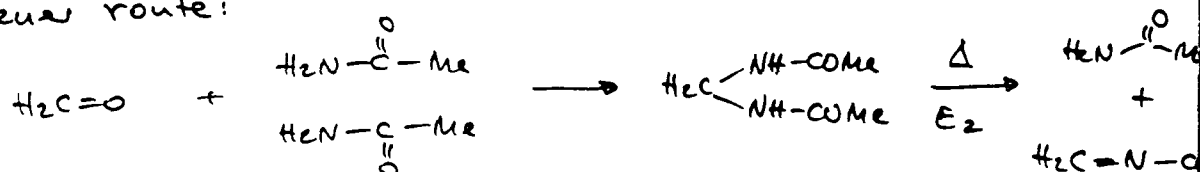
## Routes to Methyleneimines

Steglich route:

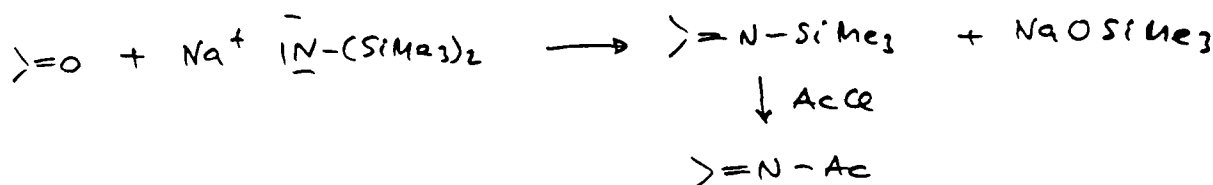


no working-up or purification possible

Brenner route:



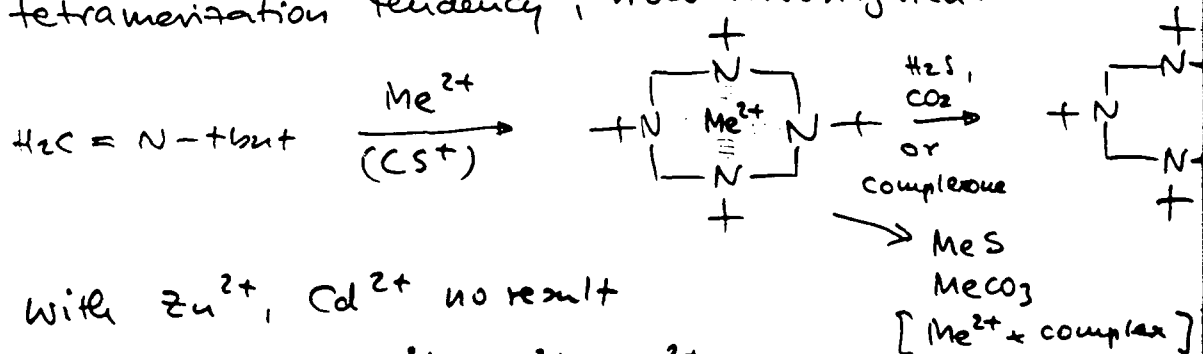
Wannagat - Württemberg route:



## Stable t-But - methyleneimine



tetramerization tendency, now investigated:



With Zn<sup>2+</sup>, Cd<sup>2+</sup> no result

now running: Co<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>



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